Characterisation of treated effluent from four commonly employed wastewater treatment facilities

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Abstract

Sewage treatment systems are a common feature across the landscape of the United Kingdom, serving an estimated 96% of the population and discharging approximately eleven billion litres of treated wastewater daily. While large treatment facilities are ubiquitous across the landscape, they are not the only method employed in domestic wastewater treatment. This study investigates whether differences in nutrient export (carbon, nitrogen and phosphorus) and organic matter composition (determined by optical indices, $SUVA_{254}$, $S_{350-400}$ and E_2:E_3) from treated effluent could be detected between four of the most common facilities employed in the treatment of wastewater across the U.K. Set in the context of the River Wylye, a small headwater catchment, treatment facilities studied included; a septic tank system, small packet treatment works, and two large sewage treatment works, one of which employed phosphorus stripping for phosphorus removal. Inorganic N and P concentrations ranging between 7.51 and 42.4 mg N l^{-1} and 0.22 and 8.9 mg P l^{-1} respectively, with DOC concentrations ranging between 1.63 and 11.8 mg C l^{-1}. Optical indices were comparable to those observed in microbially dominated endmember aquatic systems suggesting the dominance of low molecular weight material when compared to values observed across temperate aquatic systems. Combining data from both the Environment Agency and Ordinance Survey we estimate that only 25% of domestic properties in the study catchment have a corresponding Environment Agency consent/exemption permit meaning the numbers of small discharges are significantly underestimated, thus undermining efforts under current legislation to improve stream ecosystem health.

Key words: wastewater; water quality; point sources; nutrients; dissolved organic matter.

1. Introduction

Regulation and research surrounding point source discharges in the UK has focussed mainly on discharges from sewage treatment works (STW) and wastewater treatment works (WwTW) governed at present by the EU Urban Wastewater Treatment Directive or UWwTD (Council Directive 91/271/EEC). Large sewage treatment facilities are common in major urban centres of the UK with more than 9,000 wastewater treatment plants in total, 1,900 of these serving agglomerations of >2,000 population equivalent (p.e). Under the UWwTD sewage treatment facilities serving >2,000 p.e and discharging to freshwaters or estuaries are required to apply secondary treatment, defined as a treatment processes involving biological treatment with a secondary settlement or equivalent process. If discharging into coastal waters then this requirement applies at a population equivalent of >10,000. Larger agglomerations >10,000 p.e are required to apply tertiary treatment such as phosphate or nitrate removal through chemical processes or disinfection by UV irradiation or filtration membranes.

However, many properties located predominantly in rural villages or isolated areas are not connected to mains sewerage and as a result rely on private 'off grid' wastewater treatment facilities, such as septic tank systems and small packet treatment works. Existing legislation surrounding the discharge of wastewater from small point sources in England, enforceable from 2012 under the second phase of the Environmental Permitting Programme (EPP2), required sewage treatment plants discharging ≤ $5m^3$ per day (equivalent to a 25 p.e if direct into a watercourse) and septic tanks/ sewage treatment plants ≤ $2m^3$ per day or less to groundwater (12 p.e) to apply for an exemption. Systems issued with a pre-existing 'consent to discharge' from the Environment Agency were (providing they were in working order) automatically deemed exempt under EPP2. Under new regulations designed to simplify the system, this was replaced in 2015 with a system of general binding rules (GBR) detailing conditions that must be met to classify properties as exempt from requiring a permit (Environment Agency, 2015). The most significant addition being that all septic

tank systems discharging directly into a watercourse must be removed or upgraded before 2020. Subject to meeting these rules, no registration or notification of the Environment Agency is required. Figure 1 demonstrates the long-term trend (1970-2016) in discharge consents and exemptions issued in England by the Environment Agency for point sources discharges to waters, covering both domestic and commercial discharges. In total, the number of permits issued for the discharge of treated effluent since 1970 is 45,175. In addition to this over 70,000 discharge exemptions have been granted over the same period. Gaining an accurate assessment of the exact number of small sewage discharges is difficult as the impetus is on the owner to register its existence. As such it is estimated that septic tank numbers could be grossly underestimated and play a larger role in catchment nutrient budgets than currently estimated (Dudley and May, 2007).

Following implementation of the UWwTD and owing to their prevalence across the landscape the importance of large STW systems as sources of both N and P has been well studied, particularly during times of reduced instream dilution (Jarvie et al., 2006b; Neal et al., 2005; Withers et al., 2009). Discharges from 'off grid' sewerage systems have also been recently re-evaluated as to their cumulative importance in catchment N and P budgets (Withers et al., 2011). While their importance to inorganic N and P loading is well established, the specific nutrient chemistry of these different types of sewage treatment sources is understudied. Understanding their role in the delivery of dissolved organic matter (DOM) to freshwater systems, particularly those where natural organic matter is limited, such as groundwater dominated systems, is also currently lacking.

The importance of DOM in aquatic ecosystems has been widely demonstrated: it has been found to play an important role in ecosystem production (Lindell et al., 1995), mobilisation of pollutants (Aiken et al., 2011) and shielding aquatic ecosystems from harmful UV-B radiation (Hader et al., 2011) while acting as a global store of reduced carbon (Battin et al., 2009). As a result, characterisation of DOM from natural sources has received significant attention in recent literature (see, for example, Mann et al., 2014; Reyes and Crisosto, 2016; Spencer et al., 2014; Yates et al.,

2016). In contrast to natural DOM (often termed NOM), effluent-derived DOM has not received the same degree of attention and has not been extensively characterised. Research into freshwater dissolved organic carbon (DOC) from a range of environments estimates its bioavailablity to range between 23% in forested catchments to 59% in urban runoff compared to 30% in agricultural pastures (Seitzinger et al., 2002) with lower values of 4.55 % bioavailable DOC recorded draining peat catchments (Fasching et al., 2014). Recent estimates of the bioavailability of dissolved organic nitrogen (DON) and phosphorus (DOP) fractions discharged from wastewater treatment works have been found to be high, ranging between 27.9 - 60.5% and 73.7 - 75.4% for DON and DOP respectively (Qin et al., 2015). This variation is likely related to the differences in DOM composition and its specific structural properties as this varies by contributing source type. Understanding the differences between the flux of inorganic and organic nutrients from the wide variety of processes employed in the treatment of wastewater prior to direct discharge into the aquatic ecosystem is important. This will allow more comprehensive assessment of the efficiency of these small sewage treatment systems in reducing the total nutrient loading delivered to waters from these sources. It will also improve our understanding of the concentrations and composition of inorganic and organic compounds being discharged from these sources, allowing a more complete assessment of the relative importance of point sources contributing to the nutrient enrichment of waters and the consequent impacts of this enrichment on stream ecosystems.

This research recognises the differing systems for sewage treatment and discharge that commonly occur in UK catchments, and the likelihood that this will influence not only the total nutrient loading rate discharged to waters, but the specific chemistry of this loading and its likely ecosystem impacts. It investigates whether differences in inorganic and organic nutrient export from treated effluent could be detected between four of the most common facilities employed in the treatment of wastewater across the U.K. Sampling sites included a septic tank system, a small packet treatment works, a wastewater treatment plant (WwTW) with tertiary treatment for P removal, and a major sewage treatment works (STW) without tertiary P removal. To distinguish compositional differences

in DOM from effluent discharges, in addition to determination of the major N species, P fractions and DOC concentration data, optical indices including $SUVA_{254}$ (Weishaar et al., 2003), spectral slope 350-400 nm (Helms et al., 2008) and E_2:E_3 (De Haan and De Boer, 1987) were also calculated as they all have links to DOM compositional properties used to study DOM in natural systems (Jaffe et al., 2008). In addition, using data from a combination of sources we aim to accurately assess the spread of point source discharges into the receiving water body (River Wylye, UK) and generate a robust estimate the number of point source discharges currently not registered with the UK Environment Agency, but contributing to instream nutrient loading.

2. Materials and methods

2.1. Treatment facilities

Treated effluent samples were collected from four different wastewater treatment systems, all of which discharge into the upper reaches of the River Wylye, a chalk stream tributary of the Hampshire Avon, UK. Nutrient concentrations in the River Wylye are high throughout the catchment with mean annual total nitrogen and total phosphorus concentrations of 8.16 mg N l^{-1} and 126 µg P l^{-1} respectively recorded over the period 2011-2013 (Yates and Johnes, 2013). By contrast, dissolved organic nitrogen (DON), phosphorus (DOP) and carbon (DOC) concentrations are relatively low (0.766 mg N l^{-1}, 29 µg l^{-1} and 1.52 mg C l^{-1}) due to the dominance of mineral soils in the catchment. Sections of the River Wylye are designated a Special Area for Conservation (SAC), a Site of Special Scientific Interest (SSSI) and it is also listed as a groundwater Nitrate Vulnerable Zone (NVZ), designated under the European Commission Habitats Directive (92/43/EEC), the UK Wildlife and Countryside Act (1981) and the UK Nitrate Pollution Prevention Regulations (2015), in accordance with the requirements of the European Commission Nitrates Directive (91/676/EEC), respectively. Population density estimates for the catchment range from 18.5 people per km^2 in its headwater reaches to 202 people per km^2 in its lower reaches downstream of the town of Warminster.

Samples for this study were collected between October 2010 and September 2011. Treatment facility 1 (TF1) is a small septic tank system operating a basic level of primary treatment connected to a single property, and receiving domestic wastewater only. TF2 is a small packet treatment system employing a trickling filter and flocor media, which together allow the oxic conditions required for biological treatment. This site is connected to several residential properties and therefore receives waste solely from domestic sources. TF3, constructed in 1947 is a large WwTW serving the town of Warminster (population approximately 16,000) and its surrounding area. Discharges received are mainly from domestic effluent, with trade wastes contributing a further 1,500 p.e to the works. No commercial waste or septic tank waste is discharged to this works for treatment. Treatment at TF3 is split between biological filtration (40% of influent load), and additional tertiary sand filtration and activated sludge with anoxic nitrifying filtration (60% of influent load), with iron dosing employed prior to the treatment split to meet stringent Environment Agency (EA) discharge consents in order the meet the requirements of the EC Urban Wastewater Treatment Directive or UWwTD (91/271/EEC) of 1 mg-P l^{-1}. TF4 is a second major STW located just outside Warminster, which received domestic effluent and yard runoff from a military garrison. Wastewater routed to this facility receives treatment for grit removal, followed by biological filtration, with additional clarification via a humus tank prior to effluent discharge into a field drain that then feeds into the River Wylye. Due to its smaller p.e when compared to TF3, no tertiary treatment is required under the UWwTD. All location and treatment specification information for these facilities was obtained with the help of the Environment Agency and Wessex Water. For summary details including active EA discharge consents for the River Wylye, see Table 1.

2.2. Sample collection and preservation

All samples were collected in 250 ml HDPE sample bottles pre-washed with 5% HCl, and stored at 4^{o}C in the dark in transit from the field to the laboratory. Samples were returned to the laboratory on the same day as collection. On arrival at the laboratory an unfiltered aliquot was decanted for

subsequent total N and total P analysis, and placed in cold storage until analysis. A second aliquot was immediately vacuum filtered through a pre-leached 0.45µm cellulose nitrate filter to provide filtrate for dissolved organic and inorganic nutrient analysis. All samples for DOC analysis and chromophoric dissolved organic matter (CDOM) optical characterisation were separately filtered through 0.7 µm pre-combusted (450 ^{o}C) glass-fibre filters (Whatman GF/F). All samples, filtrates and digests were stored in the dark at 4^{o}C to inhibit microbial degradation with analyses completed within 24 hours of sample collection.

2.3. Methods

2.3.1. Determination of N and P and C concentrations

Inorganic nutrient analyses were conducted on a Skalar $^{++}$ multi-channel continuous flow autoanalyser (Skalar Analytical B.V., The Netherlands), set up for simultaneous determination of total oxidised nitrogen (nitrate as NO_3-N, plus nitrite as NO_2-N) hereafter referred to as Total Oxidised N (TON), total ammonium (NH_3-N + NH_4-N) and soluble reactive phosphorus (SRP, measured as PO_4-P) analyses. Determination of dissolved organic and particulate nutrient fractions were conducted on filtered and unfiltered samples digested using the persulphate oxidation method described by Johnes and Heathwaite (1992) modified for the CEM Mars Xpress microwave digestion unit. Concentrations of DOC were measured as non-purgable organic carbon determined by coupled high temperature catalytic oxidation using a Shimadzu TOC-L series analyser. The mean of three to five injections of 100 µl where the coefficient of variance (C.V) for the replicate injections was < 2% is presented here.

2.3.2. Absorbance indices

Absorbance data were obtained using a Varian Cary 300 UV-Visible spectrophotometer. Short pathlength cuvettes (10mm) were used for all samples with an absorbance value of ≥0.02 at 350 nm. Absorbance spectra were scanned over the wavelength range 200 - 800 nm at 1 nm intervals and

allowed to warm to room temperature (20 ^{0}C) prior to analysis. Average sample absorbance between 750 and 800 nm was subtracted to compensate for entrapment of any glass fibres during filtration. $SUVA_{254}$ values, a metric positively correlated to percent aromaticity of DOM using ^{13}C NMR (Weishaar et al., 2003) were calculated by dividing decadic absorbance at 254 nm by DOC concentration (mg l^{-1}) (Weishaar et al., 2003), with all absorption data presented in this manuscript expressed as absorption coefficients, as calculated below:

$$a(\lambda) = 2.303A(\lambda)/l$$

Where a(λ) is the absorption coefficient in units of reciprocal length (m^{-1}), A(λ) is raw absorbance and *l* is the cuvette pathlength (m). Spectral slope (*S*) values were calculated using a non-linear fit of an exponential function to the absorption spectrum over the range 350 - 400 nm (Helms et al., 2008).

$$a_{\lambda} = a_{\lambda\,ref}\, e^{-S(\lambda - \lambda_{ref})}$$

Where a, is the absorption coefficient, λ = wavelength (nm) and λ_{ref} is a reference wavelength (nm). Lastly, E_2:E_3 was calculated as the ratio of absorption at 250 to 366nm (De Haan and De Boer, 1987).

2.3.3. Statistical analysis

To better visualise the data and investigate correlations between variables, Principle Component Analysis (PCA), was conducted using Direct Oblimin rotation with Kaiser Normalisation for all determinands (*n, 107*). The data were tested for normality using the Shapiro-Wilk test, while homogeneity of variance was assessed by way of the Levene statistic and where appropriate, data that did not meet test assumptions were transformed using a two-step transformation method (Templeton, 2011). To assess if and how effluent nutrient concentrations varied as a function of treatment facility, a multiple analysis of variance combined with the *post hoc* Games-Howell test for unequal variances was conducted ($p < 0.05$). All data in tables are presented ± 1 standard deviation (SD). All statistical analyses were conducted using SPSS® (IBM SPSS Statistics for Windows, version

25.0. Armonk, NY: IBM Corp.) with plots generated using SigmaPlot (version 13.0; Systat Software, San Jose, CA).

Catchment reach structures and land cover were determined using the ArcGIS Hydrology toolbox (ESRI 2018. Version 10 Redlands, CA), based upon digital elevation models and land cover mapping (LCM2007) provided by the Centre for Ecology and Hydrology (U.K.). Due to the rural location of the study catchments direct census data could not be used to generate robust population density estimates. Population densities were calculated for delineated catchment reaches using Address Base Premium, the most accurate geographic database of UK addresses, properties and land areas, provided by the Ordinance Survey. Total building numbers classified as residential and occupied were multiplied by the average number of people per household (data provided for the study catchment by the Office for National Statistics) to generate a robust population estimate. This was then divided by the catchment area to provide a population density estimate (population per km^2).

The total number of properties not connected to main sewerage were estimated by subtracting the total number of residential properties identified using the Address Base Premium database with the primary classification of residential (minus residential buildings used for storage such as garages and unoccupied units etc.), from those residential properties situated in zones identified as being connected to mains sewerage (data digitised from maps provided by Wessex Water). These data were then subtracted from the EA database of consented and exempt discharges to produce a robust and best estimate of those properties not currently operating with a discharge consent or exemption.

3. Results

3.1. Point source chemical variability

Two components were identified during the PCA with eigenvalues >1 explaining 64.9% of the variance (Figure 2). DOC, TON, NH_4-N, PO_4-P, PP, DOP, and $SUVA_{254}$ all correlated with the positive

axis of component 1 with E_2:E_3 and $S_{350\text{-}400}$ correlating negatively explaining 52.7% of the variation while DON and PON correlated with the positive axis of component 2, explaining a further 12.2% of the total variation. Samples collected from the four different treatment systems can be seen in Figure 2a with component loadings shown in Figure 2b. Variables that cluster in the same space are considered to have a high degree of correlation. For example, DOC, TON, NH_4-N, PO_4-P, and DOP all loaded in the same space following PCA suggesting these variables to be highly correlated, a pattern commonly observed in monitoring of inorganic nutrients discharged from sewage treatment systems (Withers et al., 2011). The composition of the effluent discharged from the four treatment facilities monitored was found to be variable, with results from the multiple analysis of variance demonstrating significant differences in effluent concentrations as a result of treatment plant type, $F(33,215) = 48.3$, $P<0.0005$). Additional *post hoc* testing conducted to determine specific chemical differences revealed that all four treatment facilities produced significantly different inorganic nutrient concentrations, including PO_4-P, TON and NH_4-N (Figure 3). Concentrations of PO_4-P discharged from TF2 ranged between 6.82 and 10.23 mg l^{-1} (mean, 8.9 mg l^{-1} ± 0.7 SD) and were significantly higher than all other discharges (Table 2). PO_4-P concentrations in discharge from TF4 were also high compared to TF1 and TF3 discharges (mean, 4.0 mg P l^{-1} ± 1.2 SD) ranging between 0.74 mg P l^{-1} and 5.98 mg P l^{-1}. These data are consistent with monitoring conducted by the Environment Agency with mean concentrations in effluent discharged from TF4 between 1997-2001 recorded as 4.53 mg P l^{-1} ± 2.73 SD. As samples were collected from the receiving field drain, rather than from the discharge pipe itself, which was not accessible, the large range in both this data set and those data collected by the EA likely reflect dilution events from the surrounding landscape combined with a variable population in residence at any one point in time at the military garrison which TF4 serves. TF concentrations in discharge are dominated by PO_4-P at both TF2 and TF4 accounting for 77% and 86% (Figure 4a) of the total P (TP) concentration in sampled effluent. In TF1, PO_4-P still dominates the TP pool (66%) but at a lower proportion of the total concentration. This trend is reversed for TF3 with PO_4-P accounting for only 23% of the TP pool, with Particulate P (PP)

accounting for 70%of the mean annual TP concentration. Absolute concentrations in effluent discharged from TF3 however, are low (mean, 0.189 mg P l^{-1} ± 0.196 SD) and considerably lower than any discharge consent put in place by the EA (1 mg P l^{-1}, see Table 1).

Concentrations of NH_4-N demonstrate a similar pattern with the highest concentrations observed in effluent discharged from TF2 (mean, 13.9 mg N l^{-1} ± 1.0 SD), fifteen times higher than the mean concentration discharged from TF1 (mean, 0.986 mg N l^{-1} ± 0.825 SD), followed by discharge from TF3 (0.252 mg N l^{-1} ± 0.351 SD) and TF4 (0.276 mg N l^{-1} ± 1.159 SD). TON concentrations were also significantly different across all treatment types with the highest concentration discharged from TF2 (mean, 42.4 mg l^{-1} ± 1.41 SD). Inorganic N (NO_2 + NO_3-N) dominates the TN pool in both larger STW (Figure 4b) accounting for >95% of TN discharged to the River Wylye from these facilities. Discharge from both TF1 and TF2 are exceptions with NH_4-N contributing 9.4% and 22.5% of the TN concentration in discharged effluent respectively, while NH_4-N comprises 0.6% and 1% of TN in effluent discharged from TF3 and TF4, respectively. Differences in nutrient fractionation and absolute concentrations likely reflect the lower consents for ammoniacal nitrogen enforced by the EA at both TF3 (ammoniacal nitrogen consent, 3 mg N l^{-1}) and TF4 (ammoniacal nitrogen consent, 5 mg N l^{-1}) and resultant enhanced level of secondary treatment, when compared to both the septic tank (TF1) and small packet treatment works (TF2) systems which have a higher ammoniacal nitrogen consent (20 mg N l^{-1}), as detailed in Table 1.

Dissolved organic carbon concentrations are significantly elevated in effluent discharged from TF2 compared with each of the other Treatment facilities, with a mean concentration of 11.8 mg C l^{-1} (± 1.3 SD) ranging between 9.7 mg C l^{-1} and 14.8 mg C l^{-1} (Figure 3h). Elevated organic matter concentrations (DOC, DON and DOP) in the small packet treatment works discharge may be caused by inefficient mineralisation of influent nutrient loads, suggesting a system that is no longer functioning at an optimal level. No statistically significant differences in DOC concentrations were observed between discharges from TF3 and TF4, where concentrations were observed in the range

6.41 mg C l^{-1} ± 1.33 SD and 6.38 mg C l^{-1} ± 1.11 SD respectively. By contrast, TF1 demonstrated markedly lower DOC concentrations (mean, 1.63 mg C l^{-1} ± 0.46 SD) when compared to the other treatment plants.

Optical indices such as those employed during this study have been commonly used to investigate spatial and temporal shifts in DOM composition across several freshwater ecosystems (Hernes et al., 2008; Jaffe et al., 2008; Spencer et al., 2007; Spencer et al., 2014). E_2:E_3 has been used to track changes in the aromaticity and molecular size of DOM. Increases in molecular size were found to result in decreases in E_2:E_3 due to stronger light absorption at longer wavelengths (De Haan and De Boer, 1987). Data from this study demonstrated significant differences in E_2:E_3 across all treatment plants suggesting the molecular size of DOM in effluent discharges varies significantly between the 4 facility types studied. Mean values ranged from 3.99 (0.17 ± SD) at TF2 to 6.63 (0.65 ± SD) at TF1. Spectral slope, a parameter found to be inversely correlated with average DOM molecular weight (Helms et al., 2008) demonstrated a similar trend with all sites except for TF1 and TF3 demonstrating statistically significant differences (Figures 3j and k respectively). Mean $S_{350\text{-}400}$ values ranged between 13.9 x10^{-3} nm^{-1} (0.6 ± SD) at TF4 to 17.5 (0.7 ± SD) at TF3. $SUVA_{254}$, a metric positively linked to percent aromaticity of DOM using ^{13}C NMR (Weishaar et al., 2003) demonstrates less variability across treatment facilities with only TF2 showing a significantly higher mean of 2.80 mg C l^{-1} nm^{-1} (± 0.57 SD; Figure 3i). Mean $SUVA_{254}$ values across all sites compare well to systems with minimal input of terrestrial vascular plant material such as catchments with a significant groundwater signal (1.46 - 2.32 mg C l^{-1} nm^{-1}, Yates et al. 2016) and with low $SUVA_{254}$ values reported by Weishaar et al. (2003) from microbially dominated end member systems.

3.2. Estimating point source abundance on a catchment scale

The data suggest that of the >13,000 residential properties situated in the catchment 10,037 are in areas served by mains sewerage, resulting in 3,338 properties reliant on 'off grid' systems such as septic tanks, particularly in the headwaters of the catchment where dilution capacity within the

receiving water body is lower than further downstream. There are currently 493 consents/exemptions issues in the catchment suggesting that up to 2,845 smaller point source discharges are not currently registered, accounting for up to 85% of the total point sources identified in the catchment (Figure 5). In addition, of the total estimated 'off grid' systems 15% of them are within a 50m distance of the river channel, the threshold in which an Environment Agency permit is still required when draining into surface water of underlying calcareous geology.

4. Discussion

The discharge of treated effluent from large wastewater treatment facilities has been extensively studied in the literature and has been found to be an important contributor to instream loading of both nitrogen and phosphorus, contributing to eutrophic conditions in both freshwaters and further downstream in estuarine systems (Bowes et al., 2005; Jarvie et al., 2006c; Maier et al., 2009). Legislation governing point source discharges is focussed primarily on controlling the concentration of inorganic species (nitrate, ammonia and phosphate), as evident from the EA consents in place across point sources monitored during this study (Table 1), as it is concentrations of these determinands that are often elevated in treated effluent discharge (Table 2) when compared to their receiving waters.

There are over nine thousand large STW's located across the UK collecting an estimated total of eleven billion litres of wastewater daily, serving an estimated 96% of the UK population (DEFRA, 2012). In addition to this, small point source discharges from septic tank systems and small packet treatment works are a common feature in the landscape of rural catchments across the UK where connection to main sewerage is not practical, and are regarded as one of the better methods for on-site wastewater treatment. However, unlike large STW's these systems are not routinely monitored and when either poorly maintained or incorrectly sited too close to a water body, can lead to nutrient enrichment of the receiving water body (Arnscheidt et al., 2007; Withers et al., 2012). Data obtained from the Environment Agency reveal over 900,000 discharge consents issued to individual

or multiple residential properties in England for the discharge of treated wastewater. Manual identification of domestic properties not connected to mains sewerage in the River Nadder catchment, UK (Withers et al., 2012) suggested that only 1% of the septic tank systems identified in that catchment, another tributary of the Hampshire Avon, had an EA consent to discharge. If the pattern were to be repeated across all rural areas, this might indicate that the scale of nutrient loading from small point sources to UK waters may be significantly underestimated. Given that these septic tank systems frequently discharge to small headwater streams with very low dilution capacity, this may generate significant local impacts on stream ecosystem health. The data collated for the Wylye catchment, however, suggests that approximately 25% of residential properties with septic tank systems in this catchment have an EA discharge consent. The differences in these two estimates is likely to be due to differences in the methods adopted. Withers et al. (2011) used manual identification of properties through field reconnaissance, which may have resulted in a different estimate of the number of non-sewered properties, compared to the use of the Ordnance Survey digital database, manipulated within a GIS framework in this programme. The outcomes from the two studies may, therefore, not be directly comparable.

Estimates of the total number of point sources within the River Wylye catchment undertaken during this study suggested >2,800 small discharges are currently not documented by the Environment Agency, and as a result are unlikely to factor in to any calculations of nutrient loading. Translating the number of undocumented off-grid systems into a robust load estimate is difficult as final effluent concentrations discharged from small point source treatment facilities are highly variable (Jarvie et al., 2006a; Macintosh et al., 2011; Withers et al., 2011). In addition, load calculation requires several assumptions regarding both the average population per household to calculate flow rate and an assumption regarding the state of each treatment facility with respect to its condition and maintenance. However, using the EA sewage discharge calculator, this would produce approximately 778,818 m^3/year treated effluent which is not currently accounted for in current nutrient load estimates.

The inorganic nutrient fractions monitored in this study fall within the range of data reported in previous monitoring of sewage treatment systems, with TON concentrations commonly ranging between 6 and 63 mg N l^{-1} (Bowes et al., 2005; Withers et al., 2011). This is also true of soluble reactive P concentrations recorded in this study, with literature values ranging between <1 to 14 mg P l^{-1}, while ammoniacal N concentrations (NH_4-N) reported as varying between 0.03 - 72.4 mg N l^{-1} (Gill et al., 2009; Withers et al., 2011). Between-facility variations in inorganic nutrient concentrations observed in this study are a function of differences in the treatment process at each facility, and in the nutrient fractionation in the influent wastewater, together with the inclusion of P stripping at the large WwTW (TF3). While absolute concentrations of inorganic P are low in the effluent discharge from TF3, reflecting this P stripping, the data presented here suggest that PP contributed a greater proportion of the total P exported in discharged effluent from this facility, accounting for >50% of TP over the period studied. This pattern may be the result of chemical precipitation (using iron based salts) as a method to coagulate soluble P from solution, enhancing the proportion of PP present in the sample. Enhanced instream PP concentrations result in the downstream transport of particulate bound P. Reduced oxygenation at the sediment water interface, possibly caused by increased organic matter loading, may lead to the reductive dissolution of Fe(III) compounds, acting to release soluble reactive P into the water column further downstream (Evans et al., 2004). Elevated concentrations of both inorganic nutrient and organic matter in effluent discharged from TF2 indicate poor performance of this treatment facility and, while not breaching its consent, this TF is discharging a significant concentration of potentially biolabile material to a system with low dilution capacity, which is already enriched with both soluble and particulate N and P from septic tanks and combined diffuse source exports to the headwater reaches of the Upper Wylye (Yates and Johnes, 2013).

Under the UWwTD sewage treatment facilities serving populations >2,000 p.e. are required to employ secondary treatment when discharging into freshwaters and estuaries and >10,000 p.e. when discharged to coastal waters, to reduce the organic loading to waterbodies. This discharge of

organic matter from point sources may be particularly important in headwater streams with a low dilution capacity, which are also low in NOM sources in their catchments. The Upper Wylye is an example of this type of catchment, in to which these point sources discharge. This may generate locally significant and adverse impacts on stream ecosystem health, given the findings from other studies on the bioavailability of organic N and P compounds (Qin et al., 2015). Organic matter from microbial and terrestrial sources has been shown to have an important role in the functioning of aquatic ecosystems (Hood et al., 2009; Jaffe et al., 2008; Mann et al., 2014). Research into NOM has revealed how optical indices such as those calculated here can be useful in discriminatory classification of DOM from several different sources and can also reveal information regarding biotic source and biogeochemical processing of aquatic DOM (Jaffe et al., 2008; Spencer et al., 2009). Despite their prevalence in catchments across all geoclimatic conditions little research has been conducted to date to investigate the difference in organic nutrient concentrations and composition exported from sewage treatment facilities of differing scales employing different treatment processes in relation to their delivery of inorganic nutrients, routinely measured in large STW facilities, and in relation to the dilution capacity of the receiving water body. Following the targeting of improved nutrient removal at treatment facilities under the UWwTD, waterbodies are likely to require further reductions in nutrient export from both point and diffuse sources in their catchment, in order to achieve the chemical and ecological targets under the EU Water Framework Directive (WFD; 2000/60/EC). Understanding the variance in effluent discharge chemistry from differing systems will enable better targeting of mitigation, as septic tank and small packet treatment works systems, while local in scale, can discharge locally significant nutrient concentrations easily masked by diffuse nutrient loading delivered from agricultural sources within headwater catchments.

In catchments where inputs from terrestrial vegetation dominate NOM delivery to water bodies, $SUVA_{254}$ values usually range between 3 and 5.5 mg C l^{-1} m^{-1} (Spencer et al., 2012, Fasching et al., 2014; Mann et al., 2014). By contrast, in catchments with a significant groundwater influence where NOM sources are limited, $SUVA_{254}$ values can be significantly lower ranging between 1.5 and 2.3 mg

C l^{-1} m^{-1} (Yates et al. 2016). In environments where DOC concentrations are extremely low, such as in groundwater systems, $SUVA_{254}$ values are lower still ranging between 1.4 and 1.7 mg C l^{-1} m^{-1} (Shen et al., 2015; Yates et al., 2016). Mean $SUVA_{254}$ data recorded across all treatment facilities in this study ranged between 2.51 and 2.80 mg C l^{-1} m^{-1}, marginally higher than the $SUVA_{254}$ values observed from groundwater dominated systems, including in the Wylye catchment, as reported in earlier work (Yates et al., 2016). Similarly, low $SUVA_{254}$ values are mirrored by high E_2:E_3 and $S_{350\text{-}400}$ values across all sites indicating DOM with a lower molecular weight and percent aromaticity than has been reported for catchments with a higher proportion of organic rich soils.

Studies comparing DOM exported from similar treatment facilities have found little variation in weight-averaged molecular weights of extracted DOM by size exclusion chromatography, fluorescence and absorbance spectroscopy (Quaranta et al., 2012). Monitoring of municipal wastewater treatment plants in Connecticut (USA) for example observed $SUVA_{254}$ values ranging between 2.09 - 3.04 mg C l^{-1} m^{-1}, suggesting compositional similarities between these discharges from similar point sources (Quaranta et al., 2012). While this may be a reasonable assumption for DOM discharged from large wastewater treatment facilities with similar influent sources, smaller discharges have different treatment processes and are often maintained less effectively, if at all. This is likely to change the DOM composition in effluents discharged from these facilities. It is evident from data observed in this study that the pool of DOM discharged from the four different wastewater treatment facilities differ greatly from observed DOM quality metrics ($SUVA_{254}$, $S_{350\text{-}400}$) typically reported for riverine samples (Yates et. al, 2016). The input of potentially labile material from treated effluent may also lead to enhanced instream degradation of recalcitrant NOM present in aquatic systems. While such processes are well documented in soils, less work has been conducted in aquatic systems however, Steen et al. (2016) found the amendment of with labile protein + phosphorus resulted in up to a 100% increase in remineralisation rates of degraded, phytoplankton derived organic matter. Given the inorganic and organic nutrient concentrations in addition to the DOM compositional measurements observed during this study and the source areas

associated with treated wastewater is it reasonable to assume this mechanism may also occur in natural aquatic systems impacted by treated wastewater.

5. Conclusion

The nutrient speciation and CDOM data reported here point to marked differences in the quantity and character of nutrient fractions discharged to the Wylye from four of the most common sewage treatment facilities found across the U.K. This is relevant as increasing rates of urbanisation leading to increased demand for sewerage infrastructure may cause additional input of potentially labile DOM into rural and urban catchments, shifting NOM composition and potentially impacting ecosystem function and health. Urbanised watersheds with high population densities have been found to produce DOM with a distinct composition when compared to natural/semi-natural systems (Williams et al., 2016) with urban water DOM found to be dominated by anthropogenically derived DOM compounds with reduced $SUVA_{254}$ values, inferring a reduced aromatic component of the DOM pool (Hosen et al., 2014). NOM characterisation using absorbance and fluorescence techniques often distinguishes between terrestrial and microbial end members when characterising instream DOM, based on studies of catchments dominated by autochthonous or allochthonous sources (Cory and McKnight, 2005). In this earlier research the assumption is that most systems will sit somewhere on this spectrum. It is important however, to have an understanding how these indices may be affected by the input of treated wastewater from different types of treatment systems to freshwaters. As evidenced in this study, wastewater DOM has similar optical properties to those reported for microbially produced DOM in both running and standing freshwaters. As such, where wastewater is discharged to waterbodies it may not be possible to distinguish autochthonous production by in situ microbial communities from allochthonous discharges to the river from point sources in its catchment.

The discharge of elevated concentrations of both inorganic and organic nutrients from sewage treatment facilities may thus undermine efforts under current legislation to improve stream

ecosystem health through mitigation targeting diffuse source pollution from agriculture under the EU WFD and P stripping at major WwTW under the EU UWwTD. To address this gap in the science evidence currently underpinning policy, further research to investigate both the quantity and composition of DOM exported to waterbodies from the wide variety of treatment facilities operating is clearly needed along with measurements of stream ecosystem responses across a gradient of NOM concentrations. This would shed light on the relative importance and ecosystem functional impact of such off-grid point source discharges to aquatic ecosystems.

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Table and figure titles

Table 1. Technical specification of sewage treatment facilities sampled, including Environment Agency discharge consents.

Table 2. Mean determinand concentrations ± 1 SD in parenthesis for all samples collected from the four sewage treatment facilities.

Figure 1. (a) Number of discharge consents issued for individual/multiple properties and waste water treatment works (England, 1970-2015) and (b) Number of exemptions issued for discharge of sewage to surface waters (≤ 5m^3/day) and groundwater (≤ 2m^3/day). Data sourced from the Environment Agency.

Figure 2. (a) Correlation biplot from principle component analysis on chemical and optical determinands, showing principle component 1 and 2 with data grouped by treatment facility, (b) factor loadings. Clustering of variables indicates a high degree of intercorrelation.

Figure 3. Mean values for determinands from: (1) TF1 (2) TF2 (3) TF3 (4) TF4. Error bars indicate mean standard error (MSE). Differing lowercase letters above bars indicate significant differences among point source discharges as determined by *post hoc* Games-Howell test ($p < 0.05$), bars with the same letter demonstrate no significant difference.

Figure 4. Nutrient concentration breakdown for all four treatment discharges showing (a) phosphorus fractions as a percent of Total P concentration (b) nitrogen speciation as a percent of total N concentration.

Figure 5. Distribution of (a) properties classified as residential connected and not connected to mains sewerage and (b) EA issued discharge consents and exemptions in the River Wylye catchment.

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